Calorimetric and spectroscopic studies of Eu(III) complexation with tetramethylmalonamide and tetramethylsuccinamide in acetonitrile and dimethylsulfoxide

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Abstract

The complexation of Eu(III) with two N,N,N',N'-alkyl-substituted diamide ligands, tetramethylmalonamide (TMMA) and tetramethylsuccinamide (TMSA), was studied in organic solvents using titration calorimetry, FT IR and luminescence spectroscopy. The formation constants and enthalpy changes of the complexation were determined in pure acetonitrile and in acetonitrile containing small amounts of dimethyl sulfoxide (DMSO). It was observed that TMMA forms stronger complexes with Eu(III) than TMSA in the latter systems, which is attributed to the structural difference between TMMA and TMSA and an entropy effect. The effect of Eu(III) solvation by DMSO on the formation of the Eu(III)–diamide complexes is also discussed. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

There has been significant interest in recent years in the studies of alkyl-substituted amides as alternative extractants to organophosphorus compounds for actinide separation [1–6]. Alkyl-substituted amides are effective in extracting actinides, either used alone [7–9] or with β-diketones in synergistic extraction [10]. Back extraction of actinides from the amide-containing organic solvents is relatively easy. The products of radiolytic and hydrolytic degradation of amides are less detrimental to separation processes than those of organophosphorus compounds. In addition, the amide ligands are completely incinerable, which implies that the amount of secondary wastes generated in nuclear waste treatment could be significantly reduced [5,6,11,12].

Numerous studies have been conducted on the solvent extraction of actinides and lanthanides by monoamides [13–16] and diamides [9,17–29]. While most of these are focused only on the determination of distribution coefficients, a few recent studies [9,25–29] do provide information that helps to understand the effect of ligand structure on the metal extraction. For example, Byers et al. [25] determined the crystal structure of the complex between La(III) and tetraethyl-malonamide and demonstrated that the ligand is bidentate in the complex. Using solvent extraction and crystal structure analysis, Chan et al. [9] and Spjuth et al. [26] found that N,N'-dimethyl-N,N'-diphenyltetra-decylmalonamide (DMDPHTD) is a good extractant, because the O=C···C=O torsion angle of the ligand is small so that only a small conformational change is required to form the metal complex. Based on the results of an NMR study, Lefrançois et al. [27] reported that the bulkiness of substituents on the nitrogen and the central carbon lowers the rotation barriers of malonamides and thus affects the interactions with metal. Ionova et al. [28] and Rabbe et al. [29] used semi-empir-

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ical calculations to correlate the degree of metal extraction with the ligand structure. These studies have demonstrated that the structural variations, such as the substituents and the length of the carbon chain, have a great influence on metal extraction. To develop effective processes using amides for the separation of actinides, systematic studies are needed to understand the nature of the metal–amide binding, the solvent effect, and the correlation between the structure of amides and their binding affinity to actinides.

The distribution coefficients reported in the literature are a good measure of the effectiveness of the studied amides in extracting actinides under a particular set of experimental conditions. However, they are of limited use in revealing the relationship between structure and binding affinity because the extractions were performed under different conditions and a meaningful comparison between the data is difficult. In addition, solvent extraction involves not only the formation of metal–extractant complexes, but a mass partition process between the two phases as well. The latter process depends on the solubility of the metal–extractant complexes in the organic phase. As a result, the distribution coefficients do not exclusively depend on the binding affinity of the extractant to the metal ions and may not necessarily be a good measure of the metal–extractant binding strength. For the purpose of developing a structure–function relationship, a set of binding constants for a series of structurally related ligands, measured in the organic phase and under identical conditions (same solvent, temperature, ionic strength and media), is needed.

We have recently started systematic investigations on the complexation of Eu(III) with a family of structurally-related diamide ligands in organic solvents. Diamides are selected for the investigations because they show higher extractability than monoamides owing to their chelating ability [25], and there are more structural variations in diamides than in monoamides that could affect the binding affinity to metal ions. The diamides under investigation are grouped into three series for comparison:

1. N,N,N',N'-tetramethylmalonamide and N,N,N',N'-tetramethylsuccinamide, where the length of the carbon chain between the two amide groups changes;
2. N,N,N',N'-tetramethylmalonamide, N,N-dimethyl-N',N'-dibutylmalonamide, N,N,N',N'-tetra(isopropyl)malonamide, and N,N,N',N'-tetrahexylmalonamide, where the substitution on the nitrogen atoms changes;
3. N,N,N',N'-tetramethylmalonamide, N,N,N',N'-tetramethyl-methylmalonamide, and N,N,N',N'-tetramethyl-dimethylmalonamide, where the substitution on the central carbon atom changes.

The objective of these investigations is to experimentally obtain a set of comparable formation constants of the Eu(III)–diamide complexes in an organic phase and correlate the trend of binding strength with the change in the structure of the diamides. To achieve this objective, various experimental techniques were tested and different solvent systems were surveyed. A combination of titration calorimetry and spectroscopic techniques was found to be appropriate for these studies. Calorimetry was used to obtain the formation constants and the reaction enthalpy while laser-induced luminescence and FT IR spectroscopies were used to provide insight into the nature of the coordination and the substitution of solvent molecules with diamide ligands.

As is discussed elsewhere [30–34], simultaneous evaluation of formation constants and reaction enthalpy by calorimetry requires that the magnitudes of the formation constants and the reaction enthalpy are within certain limits. On one hand, if both the formation constants and the enthalpy are too small, it is difficult to observe the heat associated with the complexation and calculate these values from the titration thermogram. On the other hand, if the formation constant is above $10^{5.5}$, while enthalpies may be accurately calculated, the titration thermogram does not have sufficient curvature to allow the calculation of formation constants. As a result, a solvent suitable for these studies should be the one in which the complexation of Eu–diamide is moderately strong (ideally the formation constants ranging between 1 and $10^{5.5}$). Besides, it should provide good solubilities for all the components (Eu salts, diamides, Eu–diamide complexes, and the background electrolyte). In the present study, numerous solvents with wide ranges of Gutmann donor numbers (DN) [35,36] and dielectric constants were tested. Unfortunately, some did not provide good solubility for the components (e.g. ethanol or dioxane), others did not meet the requirement by calorimetry — the complex formation is either too weak (e.g. in pure dimethylsulfoxide) or too strong (e.g., in pure propylene carbonate or acetonitrile) to allow the evaluation of formation constants. Finally, a binary mixture of acetonitrile (AN) and small amounts of dimethylsulfoxide (DMSO) was selected as the solvent for our studies, because the presence of small amounts of DMSO (DN = 29.8) in AN (DN = 14.1) enables us to 'adjust' the strength of Eu–diamide complex so that both the formation constants and the reaction enthalpy can be calculated from the calorimetric thermograms. Besides, there is a considerable amount of information in the literature on lanthanide(III)–DMSO–AN systems [37–40] that allows a thorough understanding of metal solvation in this solvent. The constants obtained in this solvent may probably be considered 'conditional', because the reference state is neither pure AN nor pure DMSO, and the magnitude of the observed constants is the result of the competition between the diamides and DMSO and is thus dependent on the concentration of

DMSO. Nevertheless, these constants are valuable because they are obtained in the same solvent (i.e. at a fixed concentration of DMSO) and are comparable. The order of the constants reflects the effect of structural changes in the diamides on the binding affinity to metal ions.

To further understand the data obtained by calorimetry and provide insight into the nature of Eu–diamide coordination, measurements with laser-induced luminescence and FT IR spectroscopies were performed for some systems. With laser-induced luminescence spectroscopy, the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III) relative to the intensity of the magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$) was followed. FT IR measurements were performed to follow the changes in the vibrational spectra of the diamides (mainly the C–O stretching mode) and DMSO (the S–O stretching mode) upon coordination. By taking advantages of the comprehensive information on the DMSO–AN system from Bünzli's group [37–40], the replacement of DMSO by diamides was quantified.

As the first results of a series of systematic investigations on Eu–diamide complexation, this paper presents the results on the complexation of Eu(III) with N,N,N',N'-tetramethylmalonamide (TMMA) and N,N,N',N'-tetramethylsuccinamide (TMSA) in pure AN, pure DMSO, and AN containing small amounts of DMSO.

2. Experimental

Extreme care was taken to obtain and maintain the lowest water content in the systems throughout the experiments by working under an inert atmosphere of dry nitrogen or argon. Solutions of anhydrous AN, DMSO, and AN containing small amounts of DMSO were prepared in a controlled atmosphere chamber or a plastic bag filled with dry nitrogen or argon. Before being introduced into the chamber, the apparatus and nonvolatile samples were degassed in a transport that was evacuated and purged with dry nitrogen or argon at least three times. All the experiments were conducted at 25°C and in an ionic medium of 0.1 M perchlorate.

2.1. Chemicals

Fresh anhydrous solvents (unopened bottles), including AN (Aldrich, water content < 0.005%), DMSO (Aldrich, water content < 0.005%), were used for the experiments without further treatment.

Tetraethylammonium perchlorate was prepared by adding tetraethylammonium hydroxide (Aldrich) to a dilute solution of perchloric acid until neutrality was reached. After water evaporation, the crude salt was purified by repeated crystallization from CH_3OH fol-

lowing the procedures previously published [41]. The recrystallized salt was then dried by heating at 110°C under high vacuum for 24 h. The purified anhydrous tetraethylammonium perchlorate was used to make all the working solutions 0.1 M in perchlorate.

Europium perchlorate was prepared by dissolving europium oxide (Aldrich, 99.99%) in perchloric acid. The amount of perchloric acid used was slightly in excess (pH 4.5–5) with respect to the stoichiometric ratio of 3:1 ([perchlorate]: [Eu]). Extreme precautions must be taken to avoid using large or even moderate excess of perchloric acid because this can be the origin of serious accidents [42]. Evaporation of water at temperatures below 80°C resulted in a hydrated compound, $Eu(ClO_4)_3(H_2O)_x$. This compound was dehydrated by heating gradually from 50 to 120°C under high vacuum (that gradually reached 10^{-5} to 10^{-6} torr) for about 2 weeks. Repeatedly, during dehydration, the solid compound was transferred into the dry box and made into a powder form. It was ascertained that this procedure was adequate to obtain an anhydrous compound free from perchloric acid (the pH of a concentrated aqueous solution of the salt was found to be ~5). The water content in the solid perchlorate was determined with a Metrohm 684 KF Coulometer. The anhydrous salt was later used for preparing the stock solutions ([Eu] ~ 33 mM) in AN, DMSO, or AN containing small amounts of DMSO. The quantity of Eu in the solid salt and in the stock solutions was determined by complexometry with EDTA [43]. To further confirm that the Eu in the stock solutions was sufficiently dehydrated and the interference by water with the Eu-diamides complexation was negligible, laser-induced luminescence spectroscopy was used to determine the luminescence lifetime of Eu in the stock solution. A luminescence lifetime of 1.5 ms was observed, which suggested that there were essentially no water molecules in the primary coordination of Eu(III), based on the correlation between the excited state lifetime and the number of water molecules in the first coordination sphere of Eu(III) [44,45]. Working solutions of Eu were prepared by appropriate dilution of the Eu stock with 0.1 M tetraethylammonium perchlorate.

Tetramethylmalonamide (TMMA) and tetramethylsuccinamide (TMSA) used in this work were supplied by Drs M. Alnajjar and B. Rapko of the Pacific Northwest National Laboratory. The compounds were characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and GC–MS. Their purity was estimated to be > 99%. Stock solutions of the two diamides (usually 300–400 mM) were prepared by dissolving weighed amounts of TMMA or TMSA in the appropriate solvents.

Three mixture solvents with AN containing small amounts of DMSO were prepared for this study. In two of the mixture solvent systems, the molar ratios of

DMSO to Eu were maintained at 5.0 and 7.2, respectively, by either adding a calculated amount of DMSO into the Eu(III) stock solution in AN or using a well characterized adduct compound, $Eu(DMSO)_{7.2}(ClO_4)_3$, to prepare the Eu stock solution. The adduct compound (MW = 1013.1) was prepared according to the procedures described elsewhere [46] and characterized by elemental analysis and complexometry (for the Eu content). The third mixture solvent was 10.0% (w/w) DMSO–AN, which was prepared by weighing and mixing calculated amounts of DMSO and AN.

2.2. Titration calorimetry

All calorimetric experiments were carried out at $25.0 \pm 0.1°C$ with either a Tronac precision titration calorimeter, Model 87-558 or an isoperibol calorimeter (Calorimetry Sciences Corp., CSC), both equipped with a 25 ml titration vessel. For the Tronac calorimeter, the cover of the titration vessel and its connection to the calorimeter were modified in order to make a gasproof closure possible. Both the vessel and the piston burette were filled inside a controlled atmosphere chamber (Braun model MB 150B-G-I), joined together, taken out of the chamber, and connected to the calorimeter for measurements. For the titrations performed with the CSC isoperibol calorimeter, operations including filling the burette with the ligand solutions and loading the Eu solutions in the titration cup were all carried out in a controlled atmosphere chamber or a plastic bag filled with dry nitrogen or argon.

The heats of formation of the Eu(III) complexes with TMMA or TMSA were determined by adding a ligand solution of concentration $C_L{}^0$ at a constant rate (0.2– 0.4 ml min^{-1}) from the burette to an Eu solution of concentration $C_M{}^0$ in the reaction vessel. $C_L{}^0$ is usually in the range 300–500 mM and $C_M{}^0$ in the range 7–33 mM. For each titration run, n experimental values of the total heat produced in the reaction vessel ($Q_{ex,j}$, $j = 1$ to n) were calculated as a function of the volume of the added titrant. These values were corrected only for the heat of dilution of the titrant ($Q_{dil,j}$), which was determined separately, because the heat of dilution of the titrate was found to be negligible in the metal concentration range used. The net reaction heat at the jth point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. Two quantities were then defined and calculated from the net reaction heat: one is the total heat per mole of metal, $\Delta h_{v,M}$, calculated by dividing the net reaction heat with the number of moles of metal in the calorimeter vessel; the other is the stepwise heat per mole of ligand, $\Delta h_{v,L}$, calculated by dividing the stepwise net reaction heat ($q_{r,j} = Q_{r,j} - Q_{r,j-1}$) with the number of moles of ligand added in the jth step [47,48]. The formation constants of the identified complexes, the enthalpy and entropy changes of the complexation

were calculated by using a fortran program MQF90 [49] with $q_{r,j}$ or $\Delta h_{v,M}$ as the error-carrying variables.

2.3. FT IR spectroscopy

FT IR spectroscopy was used to study the interactions between Eu(III) and diamides in AN containing DMSO. The IR spectra were recorded under dry-air purge at $25 \pm 1°C$ on a Nicolet 5SXC FT IR spectrometer with a 2 cm^{-1} resolution and 256 scans. Cells with barium fluoride windows (optical path ~ 33 μm) were used. The quantitative measurements were made with a single cell, the exact thickness of which was determined by the interference fringe method [50]. The cells were filled with the sample solutions in the controlled atmosphere chamber, tightly closed, and transferred into the spectrometer with a sealed container. The spectra of pure AN and the sample solutions were recorded separately, ratioed against the background and converted to absorbance units. Successively, the AN spectrum was numerically subtracted from the sample solution spectra to obtain the difference spectra. For quantitative analysis, the absorbances of the peaks were evaluated by deconvolution of the difference spectra. A Marquartdt non-linear regression program was used to deconvolute the spectra into individual line bands, assuming Lorentzian line shapes [51,52].

2.4. Laser-induced luminescence spectroscopy

Luminescence measurements were performed with a standard 1 cm quartz fluorometer cell. The excitation and emission spectra of Eu solutions were recorded using a SPEX 1680 0.22 m Double Spectrometer. The excitation spectra were obtained by monitoring the intensity of the $^5D_0 \rightarrow {}^7F_2$ band at around 616 nm while the emission spectra were obtained from excitation of the $^7F_0 \rightarrow {}^5L_6$ band at 395 nm. The selective excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ band and the luminescence lifetime of Eu were obtained with a pulsed laser system consisting of a Continuum NY61-20 laser and a Lambda LPD 3000 Pulsed Dye Laser. The pulsed (20 Hz) 532 nm output of the Nd-YAG laser was used to pump a methanolic solution of Rhodamine 6G in the Dye Laser equipment. The $^7F_0 \rightarrow {}^5D_0$ excitation spectra were recorded by scanning the dye laser continuously through the absorption band around 580 nm with a computer-controlled stepping motor while monitoring the emission at 616 nm. The light emitted was detected by a photomultiplier tube after passing through a SPEX 270 M monochromator. For the measurements of luminescence lifetime, the signal was recorded with a digital scope and analyzed with an IBM PC computer. The laser pulse energy at 580 nm was about $15 - 20$ mJ and the pulse width was in the nanosecond range.

3. Results and discussion

3.1. Eu(III)–TMMA and Eu(III)–TMSA in pure acetonitrile

3.1.1. Calorimetry

Calorimetric experiments were performed to study the complexation of Eu(III) with TMMA and TMSA in pure AN. For TMMA, three titration runs were made

Fig. 1. $\Delta h_{\mathrm{v,M}}$ and $\Delta h_{\mathrm{v,L}}$ as a function of the ligand to metal ratio ($C_{\mathrm{L}}/C_{\mathrm{M}}$) in pure AN. (A) Eu(III) + TMMA: $C_{\mathrm{M}}^0 = 33.3$ mM (+), 16.7 mM ($\bigcirc$), 8.33 mM ($\square$). (B) Eu(III) + TMSA: $C_{\mathrm{M}}^0 = 16.8$ mM ($\bigcirc$), 8.33 mM ($\square$).

with C_{M}^0 ranging from ca. 8 to 33 mM, respectively. For TMSA, only two runs with C_{M}^0 ca. 8 and 17 mM were made. The results are shown in Fig. 1 in the form of $\Delta h_{\mathrm{v,M}}$ and $\Delta h_{\mathrm{v,L}}$ as a function of the ligand to metal ratio ($C_{\mathrm{L}}/C_{\mathrm{M}}$). As shown in Fig. 1, the titration results at different C_{M}^0 for TMMA–Eu and TMSA–Eu completely overlap, indicating that AN is a leveling solvent for these systems and unable to differentiate the binding strength between TMMA and TMSA. For both TMMA and TMSA, the total heat per mole of metal, $\Delta h_{\mathrm{v,M}}$, increases nearly proportionally with the increase in $C_{\mathrm{L}}/C_{\mathrm{M}}$ up to $C_{\mathrm{L}}/C_{\mathrm{M}} = 4$ and then becomes constant when $C_{\mathrm{L}}/C_{\mathrm{M}} > 4$. The thermograms do not show sufficient curvature, indicating that both TMMA and TMSA form up to 4 strong complexes with Eu(III) (ML_i, $i = 1$–4). Consequently, it is not possible to calculate and compare the formation constants of the Eu–TMMA and Eu–TMSA complexes in pure AN. However, the enthalpy of complexation can be accurately determined and the lower limit of the stepwise constants ($K_i = [\mathrm{ML}_i]/([\mathrm{ML}_{i-1}][\mathrm{L}])$, $i = 1$–4) can be estimated to be $10^{5.5}$ (Table 1).

3.1.2. Luminescence spectroscopy

Luminescence spectroscopy was used to provide further insight into the interaction between Eu(III) and the diamides. As pointed out by Bünzli et al. [53], the forbidden f–f excitation bands of Eu(III) in the UV region are usually weak and little affected when Eu(III) is complexed with the diamides. The maximum absorption is at about 394 nm ($\varepsilon \sim 2.75$ mol^{-1} cm^{-1}). However, the luminescence emission bands in the visible region, originating from electronic transitions from the lowest excited state, $^5\mathrm{D}_0$, to the ground state manifold, $^7\mathrm{F}_J$ ($J = 0$–6), are sensitive to the changes in the first coordination sphere. These features are observed in the luminescence emission spectra (Fig. 2) of Eu–TMMA and Eu–TMSA complexes in pure AN.

The emission spectra show significant changes as the ratio of $C_{\mathrm{L}}/C_{\mathrm{M}}$ ([TMMA]/[Eu] or [TMSA]/[Eu]) increases (Fig. 2). The changes can be summarized as follows. (i) The relative intensity of the forbidden transition $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_0$, with respect to the intensity of the magnetic dipole transition $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$, increases sharply when $C_{\mathrm{L}}/C_{\mathrm{M}}$ increases from 0 to 1.2 and then decreases when $C_{\mathrm{L}}/C_{\mathrm{M}}$ further increases to 4. The magnetic dipole transition $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$ (around 590–600 nm) is often used as the internal standard for intensity comparison because it is not affected by the environment of the fluorescent ion [37,53]. (ii) The relative intensity of the hypersensitive $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$ transition (around 620 nm) increases significantly with respect to the intensity of the $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$ transition when $C_{\mathrm{L}}/C_{\mathrm{M}}$ increases from 0 to 4, but remains constant when $C_{\mathrm{L}}/C_{\mathrm{M}} > 4$. These changes are associated with the change of the coordination environment of Eu(III) from a weaker ligand field

Table 1
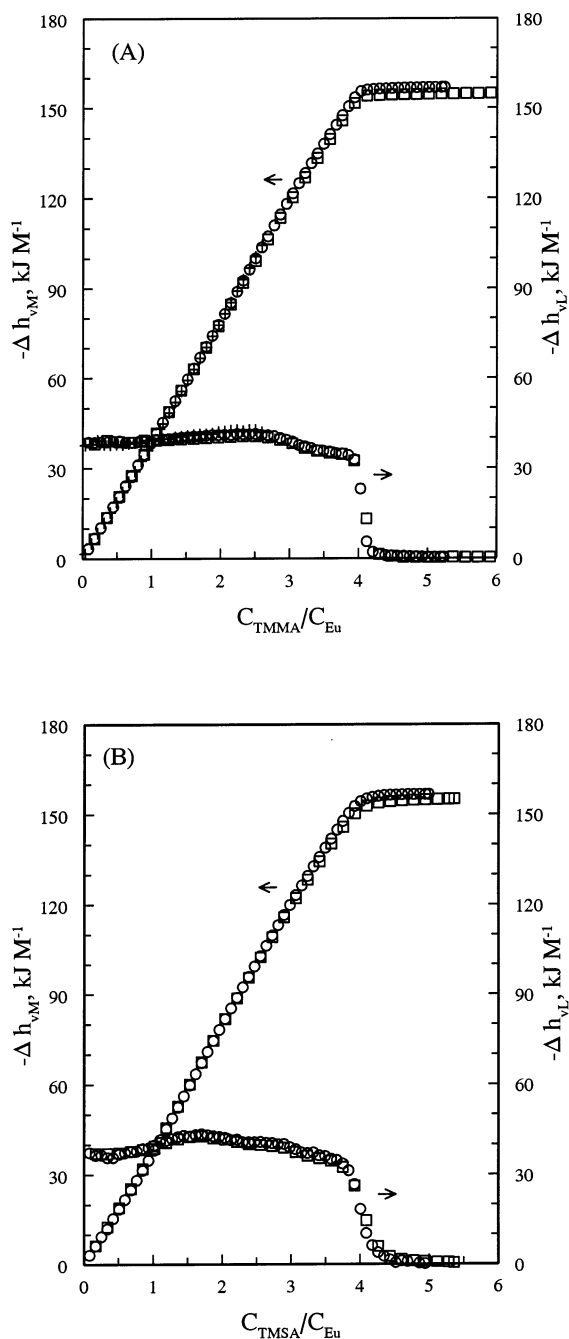The overall formation constants [a], enthalpies and entropies of Eu(III) complexation with TMMA and TMSA ($T = 25°$C, ionic medium: 0.1 M tetraethylammonium perchlorate)

Solvent–complex ML_j		Eu(III)–TMMA			Eu(III)–TMSA		
		$\log \beta_i \pm 3\sigma$ (M^{-j})	$\Delta H \pm 3\sigma$ (kJ mol^{-1})	$\Delta S \pm 3\sigma$ (J K^{-1} mol^{-1})	$\log \beta_i \pm 3\sigma$ (M^{-j})	$\Delta H \pm 3\sigma$ (kJ mol^{-1})	$\Delta S \pm 3\sigma$ (J K^{-1} mol^{-1})
Pure AN	ML_4	≥ 22 [b]	-155.5 ± 1.0		≥ 22 [b]	-155.5 ± 1.0	
AN DMSO/Eu = 5	ML	3.9 ± 0.6	-40.3 ± 0.20	-61 ± 12	3.3 ± 0.5	-42.2 ± 2.4	-78 ± 18
	ML_2	6.7 ± 1.0	-62.0 ± 0.11	-80 ± 20	5.4 ± 0.9	-67.0 ± 2.1	-121 ± 24
	ML_3	8.7 ± 0.9	-32.0 ± 0.8	59 ± 20	6.8 ± 1.4	-21.2 ± 5.0	59 ± 44
AN DMSO/Eu = 7.2	ML	2.48 ± 0.05	-32.0 ± 0.9	-60 ± 4	2.39 ± 0.05	-31.6 ± 0.9	$-60 \pm (4)$
	ML_2	4.22 ± 0.13	14 ± 4	128 ± 16	4.07 ± 1.4	21 ± 6	148 ± 23
	ML_3	6.01 ± 0.20	4.0 ± 0.8	128 ± 7	5.95 ± 0.19	-2.1 ± 1.2	107 ± 8
10% DMSO in AN DMSO/Eu ≥ 30	ML	1.34 ± 0.04	22.4 ± 0.8	101 ± 3	0.77 ± 0.08	25.8 ± 3.3	101 ± 13
Pure DMSO	ML	< 0			< 0		

[a] Overall formation constants, $\beta_i = [ML_i]/([M][L]^i)$. Also, $\beta_i = K_1 K_2, \ldots, K_i$, where K_i is the stepwise formation constant.
[b] Estimated value for $\log \beta_4$ based on the stepwise $\log K_i$ ($i = 1$–4) ≥ 5.5.

of pure solvent (AN) to a stronger ligand field of the amide [54], providing evidence of the strong interaction of Eu(III) with TMMA and TMSA in AN and confirming the formation of four strong complexes as observed in calorimetry.

The $^7F_0 \rightarrow {}^5D_0$ excitation band of Eu(III) is unique because both the ground state and the excited state are non-degenerate and are not split by the ligand field. As a result, only a single electronic transition between these states is allowed for each chemical environment of Eu(III). In other words, the number of components of the $^7F_0 \rightarrow {}^5D_0$ band corresponds to the minimum number of chemical species of Eu(III). This excitation band is too weak to be observed with the fluorometer, but can be studied by laser-induced luminescence spectroscopy. Using the instrumentation described in Section 2.4, the selective $^7F_0 \rightarrow {}^5D_0$ excitation spectrum was obtained for a solution of Eu–TMMA in AN after one calorimetric titration ($C_L/C_M = 5$). The spectrum is best fit with a single peak with maximum at 580.2 nm, corresponding to one Eu(III) species. Based on the results from calorimetry (Fig. 1) and the luminescence emission spectra (Fig. 2), it is very likely that this species is Eu(TMMA)$_4$.

The luminescence lifetime (τ) of the above Eu–TMMA solution was measured with the pulsed laser system. It was found that the luminescence decay was well represented by a single exponential function with a decay constant of $k = 1/\tau = 0.71$ ms^{-1}. This value is of the same amplitude as the decay constant induced by non-radiative pathways in the absence of high energy oscillators, suggesting that there are essentially no water molecules directly coordinated with Eu(III) in this solution [44,45]. This result, in turn, confirms that the precautions taken in the experimental procedure are successful in maintaining an anhydrous condition.

3.2. Eu(III)–TMMA and Eu(III)–TMSA in pure DMSO

Calorimetric experiments were performed to study the complexation of Eu(III) with TMMA and TMSA in pure DMSO. No reaction heat was observed when the Eu(III) solutions were titrated with the solutions of TMMA or TMSA. This observation is consistent with either or both of the following arguments: (i) there is no complexation between Eu(III) and TMMA or TMSA in pure DMSO (or the complex is too weak to be observed by calorimetry); (ii) the complex could be strong but the enthalpy changes are close to zero. To clarify this, the luminescence emission spectra of Eu(III) in DMSO were measured at various ratios of [TMMA]/[Eu] and [TMSA]/[Eu]. No changes in the hypersensitive transition of Eu(III) ($^5D_0 \rightarrow {}^7F_2$) were observed when the ratio increased from 0 to 10 ([Eu] = 33 mM, [TMMA] or [TMSA] = 0 to 330 mM). These results, combined with those of calorimetry, confirmed that the complexation of Eu(III) with TMMA or TMSA in pure DMSO is very weak and cannot be accurately evaluated by calorimetry. By estimation, the upper limit of the formation constants ($K_1 = [ML]/([M][L])$) in pure DMSO is 1[1].

Though the experimental results in pure AN or pure DMSO do not allow the calculation of the formation constants of Eu–diamide complexes, they provide the lower limit for the constants in AN ($> 10^{5.5}$) and the upper limit for the constants in DMSO (< 1). The formation constants in pure AN are at least 5 orders of

[1] $[ML]/[M]_{Total} = K_1[L]/(1 + K_1[L])$. If [Eu] = 33 mM, [TMMA] = 330 mM and $K_1 = 1$, $[ML]/[M]_{Total}$ is about 22%. This should result in observable changes in the hypersensitive transition of Eu(III). However, no such changes were observed.

magnitude higher than those in pure DMSO. This is understandable in terms of the difference in solvating power between AN and DMSO [35]. In fact, in a series of FT IR and fluorometric investigations of the solvation of rare-earth ions [37–40], Bünzli et al. found that when DMSO was added to an anhydrous AN solution of $Eu(ClO_4)_3$, the DMSO molecules replaced first the AN molecules from the inner coordination sphere of

the metal ion, then the perchlorate ions. When the DMSO–Eu ratio was ≥ 10, the number of ionic ClO_4^- per Eu^{3+} ion was 3. In pure DMSO the nonacoordinate species is largely predominant [37]. Evidently DMSO solvates Eu(III) much more strongly than AN. In pure DMSO, the diamides are unable to compete with DMSO for coordination of Eu(III).

3.3. Eu(III)–TMMA and Eu(III)–TMSA in acetonitrile containing small amounts of DMSO

Three solvent systems of AN containing small amounts of DMSO were used in the study. In the first two, the molar ratios of DMSO–Eu are maintained at 5.0 and 7.2, respectively. In the third one, the solvent composition was kept constant and equal to 10% (w/w) DMSO in AN. In the latter system the DMSO is in large excess with respect to Eu ([DMSO]/[Eu] ≥ 30). The objective of these studies is to determine how the "conditional" formation constants in these solvents are affected by the amount of DMSO in solution, so that a suitable mixture solvent (with a fixed amount of DMSO in AN) can be selected to allow the determination of a set of comparable formation constants for Eu–TMMA and Eu–TMSA by calorimetry. FT IR spectroscopy was used to provide further information on the solvation of Eu(III) and the nature of the Eu–diamide complexes.

3.3.1. Calorimetry

In all the three solvent systems, formation of Eu–TMMA and Eu–TMSA complexes was well observed by calorimetry. For each system, usually 3 to 4 titration runs with different C_M^0 were performed to achieve better statistics in the calculation of formation constants and reaction enthalpies. Since the titration thermograms are very similar for Eu–TMMA and Eu–TMSA in all the three systems, only the plots for Eu–TMMA are presented.

The observed reaction heats for Eu–TMMA are presented in Fig. 3 in the form of $\Delta h_{v,M}$ as a function of the ligand to metal ratio ($C_L/C_M = $ [TMMA]/[Eu]). The results obtained in pure AN are also included for comparative discussion. The plots show significant differences among the systems with different amounts of DMSO. The differences can be summarized as follows. (i) In the absence of DMSO (curves A), the reaction is strongly exothermic and the reaction heat changes proportionally with the increase of C_L/C_M from 0 to 4, indicating the formation of four strong Eu–TMMA complexes with all exothermic enthalpies. (ii) In the system with [DMSO]/[Eu] = 5.0 (curves B), the reaction is exothermic when C_L/C_M increases from 0 to 2, but becomes endothermic when $C_L/C_M > 2$. (iii) In the system with [DMSO]/[Eu] = 7.2 (curves C), the reaction is exothermic when C_L/C_M increases from 0 to 1, but

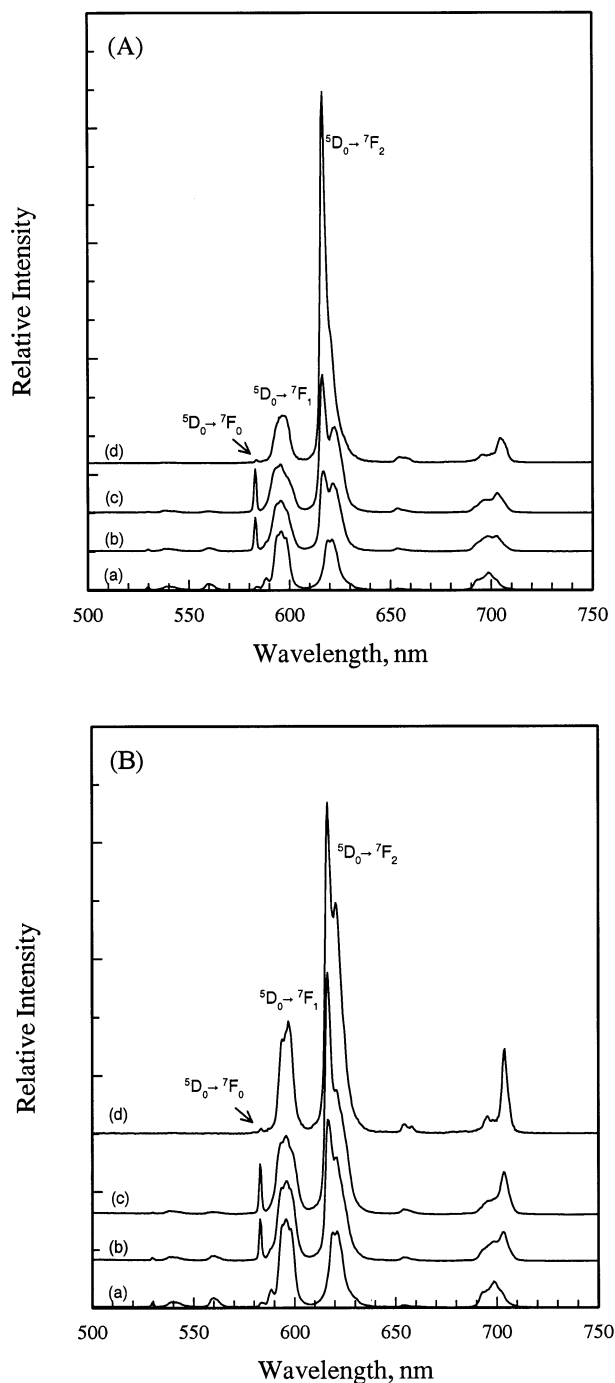Fig. 2. Emission spectra of $Eu(ClO_4)_3$ in pure AN in the presence of various amounts of diamides. $\lambda_{ex} = 395$ nm. [Eu] = 33.3 mM, $C_L/C_M = 0$ (a), 0.6 (b), 1.2 (c), ≥ 4.0 (d). (A) TMMA, (B) TMSA.
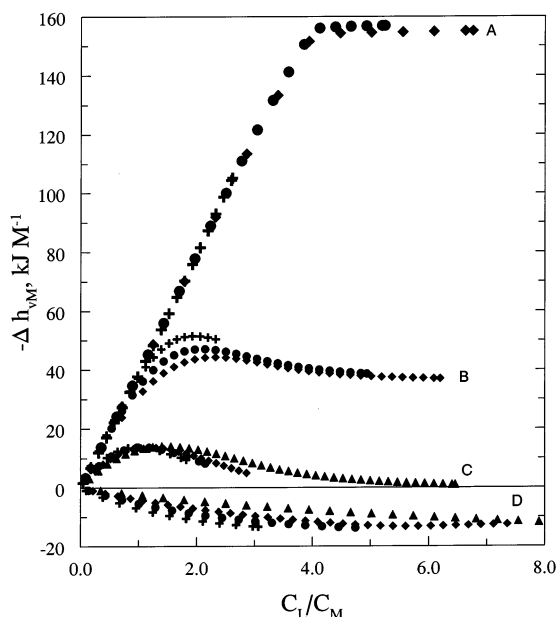
Fig. 3. Eu(III)–TMMA systems. $\Delta h_{v,M}$ as a function of the ligand to metal ratio (C_L/C_M) in AN containing different amounts of DMSO. (A) No DMSO; $C_M{}^0 = 33.3$ (+), 16.7 (●), 8.33 mM (♦). (B) [DMSO]/[Eu] = 5.0; $C_M{}^0 = 33.7$ (+), 16.7 (●), 8.34 mM (♦). (C) [DMSO]/[Eu] = 7.2; $C_M{}^0 = 33.8$ (+), 25.3 (●), 16.9 (♦), 8.44 mM (▲). (D) 10.0% DMSO, $C_M{}^0 = 34.3$ (+), 20.6 (●), 13.7 (♦), 6.85 mM (▲).

becomes endothermic when $C_L/C_M > 1$. (iv) In the system with the highest [DMSO]/[Eu] ratio (≥ 30, curves D), the reaction is endothermic from the beginning of the titration. Similar trends were observed for Eu–TMSA.

3.3.1.1. Formation constants of Eu–diamide complexes. The MQF90 program [49] was used to calculate the formation constants as well as the enthalpy for the complexation of Eu(III) with TMMA and TMSA. It was found that the least standard deviations were obtained when the titration curves B and C were modeled with three complexes and curves D with one complex, respectively. Accordingly, for the systems with [DMSO]/[Eu] = 5.0 and 7.2 (Curves B and C), formation constants and enthalpy values for three consecutive complexes, EuL, EuL$_2$ and EuL$_3$, are calculated. For the system containing 10% of DMSO (Curves D), the formation constant and enthalpy for EuL was calculated. The values for both Eu–TMMA and Eu–TMSA systems are listed in Table 1.

These results demonstrate that the amount of DMSO in acetonitrile has a significant impact on the formation of Eu–diamide complexes. When the ratio of [DMSO]/[Eu] increases from 0 to ≥ 30, the formation of Eu–diamide complexes becomes more difficult. For example, the formation constants for Eu–TMMA decrease in the order: $\log \beta_1 > 5.5$ (no DMSO); $\log \beta_1 = 3.9$ (DMSO/

Eu = 5); $\log \beta_1 = 2.48$ (DMSO/Eu = 7.2); $\log \beta_1 = 1.34$ (DMSO/Eu ≥ 30). The same trend is observed for Eu–TMSA complexation. Such trends are understandable in terms of the solvation effect on complex formation. For a given ligand, the stability of a complex is, in general, inversely proportional to the solvation of the metal ion [35]. There is literature information on metal solvation in AN and DMSO systems that could provide insight into the Eu(III) solvation in the systems of this study. For example, in a calorimetric study of metal solvation in AN–DMSO mixtures, Inerowicz et al. observed strong preferential solvation of metal ions by DMSO [55]. Such preferential solvation was quantified by Bünzli et al. [37–40]. Using FT IR to monitor the shifts in frequency and the changes in intensities of the S–O stretch (v_7) and the asymmetric C–S stretch (v_{22}), Bünzli et al. illustrated the equilibria between different solvated species. It was found that when the ratio of [DMSO]/[Eu] increases, DMSO molecules are quantitatively coordinated to Eu(III) up to a ratio of 7.7. When [DMSO]/[Eu] is in the range of 7.7 to 12, there are equilibria between species containing different numbers of coordinated DMSO molecules, Eu(DMSO)$_n$, where $n = 7$, 8 and 9. When [DMSO]/[Eu] > 12, the nonacoordinated species, Eu(DMSO)$_9$, becomes dominant with an average coordination number of 8.7 ± 0.5 [37–40]. As a result, the formation of Eu–diamide complexes in AN containing different amounts of DMSO requires replacement of different numbers of DMSO from the coordination sphere of Eu(III). Accordingly, the magnitude of the observed formation constants ('conditional' constants) reflects the competition between diamides and DMSO for coordinating Eu(III). Such competition and its effects on the formation of metal complexes are further illustrated in the following discussions on enthalpy and entropy.

3.3.1.2. Enthalpy and entropy of complexation. An examination of the stepwise enthalpy and entropy, the latter in particular, can provide additional information on the desolvation of Eu(III) upon complexation with the diamides. In general, positive entropy changes reflect a higher degree of disorder due to the complex formation while negative entropy changes suggest less perturbation in the solvation sphere of the metal upon complexation. Such entropy effect is more prominent in the formation of chelate complexes, such as the complexes of Eu(III) with diamides, because of the net increase in the number of free molecules.

Using Bünzli's quantitative descriptions of the solvation of Eu(III) in AN–DMSO mixtures, it is possible to understand the trend of the enthalpy and explain the sign and magnitude of the entropy shown in Table 1. For the 10% DMSO–AN system where [DMSO]/[Eu] ≥ 30, the primary coordination sphere of Eu(III) is saturated by DMSO (CN ~ 9) and consequently two

DMSO molecules must be removed to form the first Eu–diamide complex (EuL). The formation of EuL in this system can be illustrated as reaction Scheme I:
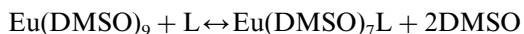
Scheme I ([DMSO]/[Eu] $\geq$ 30)	$N_{DMSO\ replaced}$	ΔH	ΔS
$Eu(DMSO)_9 + L \leftrightarrow Eu(DMSO)_7L + 2DMSO$	2	endothermic	positive

Removing the strongly solvating DMSO from the primary coordination sphere requires a significant amount of energy, resulting in weak EuL complexes and endothermic enthalpy changes (22.4 kJ mol^{-1} for TMMA and 25.8 kJ mol^{-1} for TMSA). Formation of further complexes (EuL$_2$ and EuL$_3$) is even more energy-deficient and too weak to be observed by calorimetry in this solvent system. The entropy for EuL is positive (101 J K^{-1} mol^{-1} for both TMMA and TMSA), reflecting the net gain in the degree of freedom when the diamide replaces two DMSO molecules from the coordination sphere of Eu(III). In this case, the loss of freedom of the diamide (mainly translational and rotational) is more than compensated by the concomitant gain in the entropy of two DMSO molecules free to move in the solvent.

For the system with [DMSO]/[Eu] = 7.2, there are about two 'vacant' sites (i.e. sites not occupied by DMSO but may be occupied by AN and/or perchlorate) around Eu. This allows the formation of the first

and rotational entropy of TMMA or TMSA is only in part compensated by the gain in the entropy of AN molecules, resulting in a negative net entropy for the formation of EuL.

However, when the second complex (EuL$_2$) forms in the system with [DMSO]/[Eu] = 7.2, two DMSO molecules need to be replaced and the stepwise enthalpy becomes endothermic (46 kJ mol^{-1} for TMMA and 52.6 kJ mol^{-1} for TMSA). Two DMSO molecules are set free from Eu into the bulk solvent, resulting in a gain in the degree of freedom that exceeds the loss in the translational and rotational freedom of the second incoming diamide molecule. As a result, the stepwise entropy for the formation of EuL$_2$ becomes positive (188 J K^{-1} mol^{-1} for TMMA and 208 J K^{-1} mol^{-1} for TMSA). The formation of the first two Eu–diamide complexes in this system is illustrated by reaction Scheme II. It should be noted that there are equilibria between species containing different numbers of coordinated DMSO. Thus the number of DMSO shown in the scheme denotes the average number.
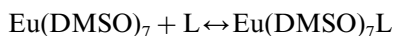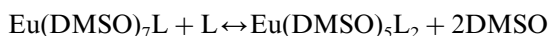
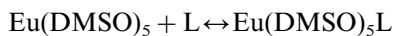| Scheme II ([DMSO]/[Eu] = 7.2)	$N_{DMSO\ replaced}$	ΔH	ΔS
$Eu(DMSO)_7 + L \leftrightarrow Eu(DMSO)_7L$	0	exothermic	negative
$Eu(DMSO)_7L + L \leftrightarrow Eu(DMSO)_5L_2 + 2DMSO$	2	endothermic	positive

Eu–diamide complex without requiring much energy in desolvation (replacing the less strongly solvating AN or perchlorate does not require as much energy as replacing DMSO). As a result, the formation of EuL is exothermic (-32 kJ mol^{-1} for TMMA and -31.6 kJ mol^{-1} for TMSA). The entropy is negative (-60 J K^{-1} mol^{-1} for both TMMA and TMSA), resulting from the loss of translational and rotational entropy of TMMA or TMSA upon chelation. Concomitantly, some AN molecules may be released from Eu into the bulk solvent, which could result in some gain in entropy. However, considering that the structuring effect of the charged metal ion on the bulk solvent does not change substantially since no charge neutralization occurs when these complexes form, it is reasonable to presume that the AN molecules set free from the coordination sphere of the metal ion upon chelation do not gain excessive entropy once in the bulk. Consequently, the loss of translational

Similarly, the results for the system with [DMSO]/[Eu] = 5.0 can be understood. In this system, there should be 3–4 'vacant' coordination sites that allow the formation of the first and the second Eu–diamide complexes without spending much energy on replacing DMSO. As a result, the formations of EuL and EuL$_2$ are exothermic (-40.3 and -21.7 kJ mol^{-1} for TMMA, -42.2 and -24.8 kJ mol^{-1} for TMSA). In addition, the stepwise entropies are negative (-61 and -19 J K^{-1} mol^{-1} for TMMA, -78 and -43 J K^{-1} mol^{-1} for TMSA), because the formation of these two complexes does not significantly perturb the DMSO in the primary solvation sphere of Eu(III). Only when the third complex (EuL$_3$) forms, the stepwise enthalpy becomes endothermic (30 kJ mol^{-1} for TMMA and 45.8 kJ mol^{-1} for TMSA), and the stepwise entropy becomes positive (139 J K^{-1} mol^{-1} for TMMA and 180 J K^{-1} mol^{-1} for TMSA) because two DMSO molecules are replaced. The formation of the three stepwise Eu–diamide complexes in this system is illustrated by reaction Scheme III:

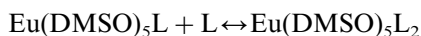| Scheme III ([DMSO]/[Eu] = 5.0)	$N_{DMSO\ replaced}$	ΔH	ΔS
$Eu(DMSO)_5 + L \leftrightarrow Eu(DMSO)_5L$	0	exothermic	negative
$Eu(DMSO)_5L + L \leftrightarrow Eu(DMSO)_5L_2$	0	exothermic	negative
$Eu(DMSO)_5L_5 + L \leftrightarrow Eu(DMSO)_3L_3 + 2DMSO$	2	endothermic	positive

To test how well the calculated stability constants and enthalpies in Table 1 represent the experimental results, the values were in turn used to simulate the calorimetric titration thermograms. As shown in Figs. 4
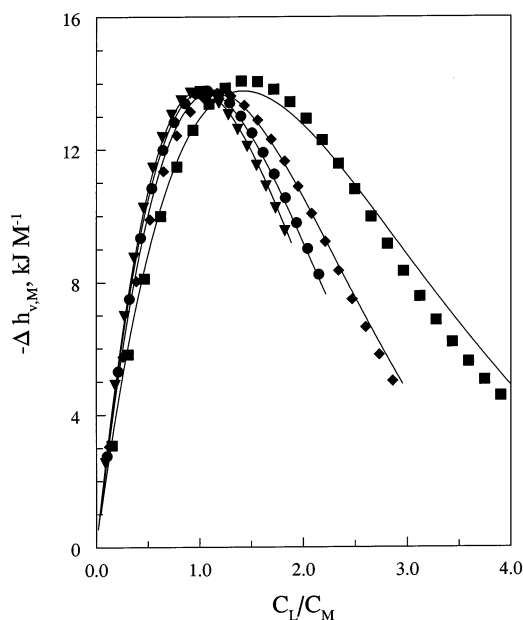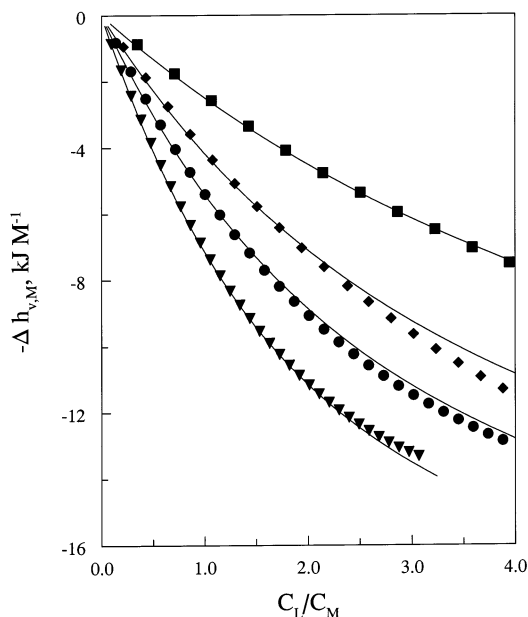

Fig. 4. Eu(III)–TMMA systems. Simulation plots of $\Delta h_{v,M}$ as a function of the ligand to metal ratio (C_L/C_M) in AN containing small amounts of DMSO ([DMSO]/[Eu] = 7.2). Points-experimentally observed; curves-calculated with the stability constants and enthalpies in Table 1. $C_M{}^0$ = 33.8 (▼), 25.3 (●), 16.9 (◆), 8.44 mM (■).

Fig. 5. Europium(III)–TMMA systems. Simulation plots of $\Delta h_{v,M}$ as a function of the ligand to metal ratio (C_L/C_M) in AN containing 10.0% of DMSO. Points-experimentally observed; curves-calculated with the stability constants and enthalpies in Table 1. $C_M{}^0$ = 34.3 (▼), 20.6 (●), 13.7 mM (◆), 6.85 mM (■).

Table 2
Assignments of selected vibrational frequencies

Wavenumber (cm^{-1})	Assignment	Reference
1102, 1091	ν_3, ClO$_4^-$	[38,56]
1060	ν_7 (S–O stretch), bulk DMSO	[37,57,58]
1103–1009	ν_7 (S–O stretch), coordinated DMSO	[37,57,58]
950	ν_{22} (asymmetric C–S stretch), bulk DMSO	[37,57,58]
961–965	ν_{22} (asymmetric C–S stretch), coordinated DMSO	[37,57,58]
1120–1200	composite bands of diamides, not resolved	

and 5, they provide good representations of the experimental data.

3.3.2. FT IR spectroscopy

The above discussions on the calorimetric results are made based on two arguments: (i) the diamide ligands are bidentate to Eu(III) and each may replace two DMSO molecules if the Eu(III) is fully solvated by DMSO (CN ∼ 9); (ii) in the systems where Eu(III) is not fully solvated by DMSO (e.g. when [DMSO]/[Eu] = 7.2 or 5.0), the formation of the first one or two Eu–diamide complexes does not require the replacement of two DMSO from the primary solvation sphere of Eu(III) by each diamide ligand. To provide experimental evidence supporting these arguments and allow a quantitative description of the desolvation of Eu(III), FT IR spectra were recorded covering the wavelength range from 846 to 4000 cm^{-1}. Two wavelength regions that are of particular interest to this study are discussed as follows. The band assignments are shown in Table 2.

3.3.2.1. Wavelength region of 1500–1700 cm^{-1}.

This is the region where the stretching bands of the carbonyl groups in diamides are observed (Fig. 6). The absorption bands around 1650 cm^{-1} could be assigned to the carbonyl stretching modes in the free TMMA (Fig. 6(A)) and TMSA (Fig. 6(B)). As the ratio of C_L/C_M ([TMMA]/[Eu] or [TMSA]/[Eu]) increases, these bands are red-shifted and appear around 1600–1630 cm^{-1}, indicating the formation of Eu–TMMA and Eu–TMSA complexes. These results are consistent with Byers' observation [25] for the complexation of La(III) with tetraethylmalonamide, where the C–O stretching mode of the free ligand was at 1645 cm^{-1} but shifted to 1613 cm^{-1} in the bound ligand. Structural analysis by X-ray crystallography indicated that the malonamide behaved as a bidentate ligand and complexed with La(III) through the oxygen atoms of the two carbonyl groups [9,25]. Edwards et al. also reported similar red-shifts of the carbonyl stretching bands when malonamides, succinamides and glutaramides formed biden-

tate chelates with neodymium, uranium and thorium [59]. Based on the literature information and the observations in the present study, it is concluded that both TMMA and TMSA form bidentate chelate complexes with Eu(III) through the two carbonyl oxygen atoms.

3.3.2.2. Wavelength region of 900–1200 cm⁻¹. This is the region where the vibrational bands of both perchlorate and DMSO are observed (Fig. 7). Fig. 7(A) and (B) show the IR absorption spectra for Eu–TMMA and Eu–TMSA in AN with small amounts of DMSO ([DMSO]/[Eu] = 7.2). Analysis of these spectra can provide quantitative information on the substitution of DMSO in the coordination sphere of Eu(III) by diamides. As C_L/C_M increases from 0.5 to 10, the intensity of the bands around 1009 and 965 cm⁻¹ (assigned to the S–O stretching and C–S stretching of the coordi-

nated DMSO, respectively) decreases while the band intensity at 1060 cm⁻¹ (assigned to the S–O stretching mode of the free DMSO) gradually increases, indicating that DMSO is repelled from the coordination sphere of Eu(III) as the Eu–TMMA or Eu–TMSA complexes form. The unresolved bands in the region of 1120–1200 cm⁻¹ are assigned to the vibrational modes of TMMA (Fig. 7(A)) or TMSA (Fig. 7(B)). The intensity of the band around 1102 cm⁻¹ (assigned to the vibrational mode of free perchlorate ions) does not show much change when C_L/C_M increases from 0.5 to 10, which suggests that few perchlorate ions are coordinated with Eu(III) and little perturbation on perchlorate occurs when the complexes of Eu–TMMA or Eu–TMSA form.

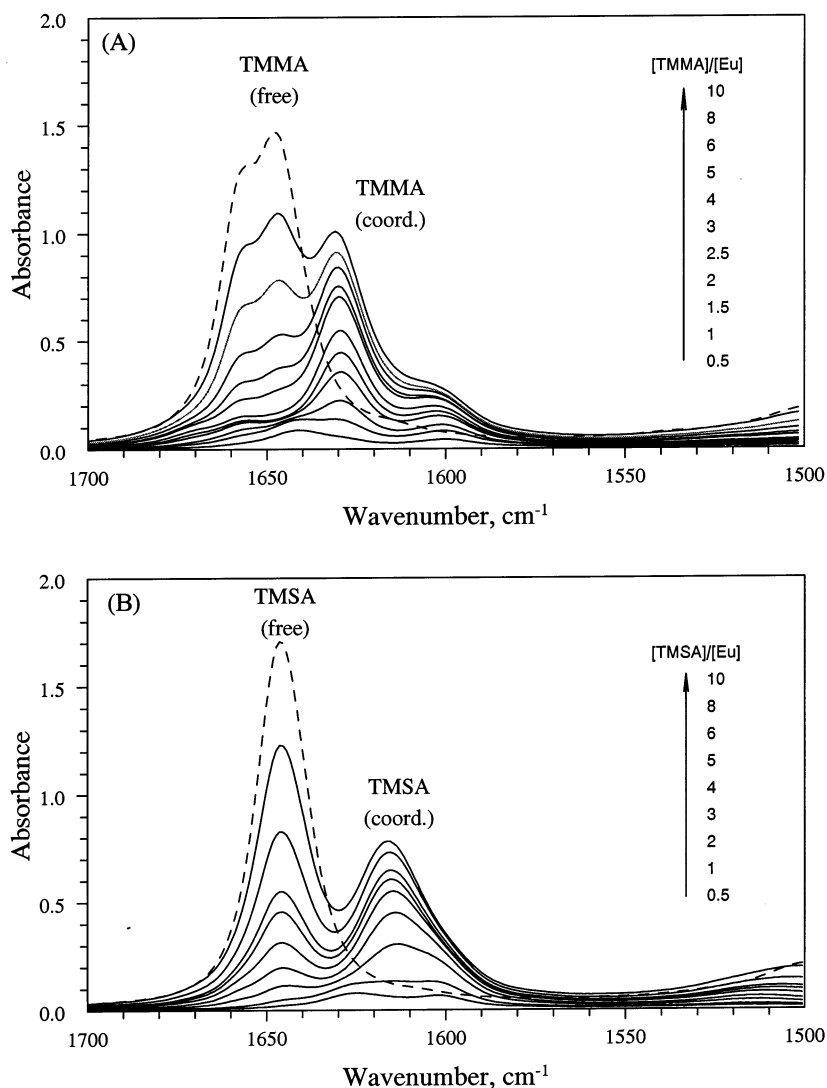Evaluation of Fig. 7(A) and (B) suggests that the S–O stretching mode at 1060 cm⁻¹ is the most suitable

Fig. 6. FT IR spectra of Eu–diamides in AN containing small amounts of DMSO ([DMSO]/[Eu] = 7.2). The spectra show the red-shift of C–O vibration frequencies upon complexation with Eu(III). [Eu] = 33.3 mM. (A) TMMA, 0–333 mM; (B) TMSA, 0–333 mM. The dashed lines in both (A) and (B) are for the pure ligand (TMMA or TMSA, 333 mM) in AN.
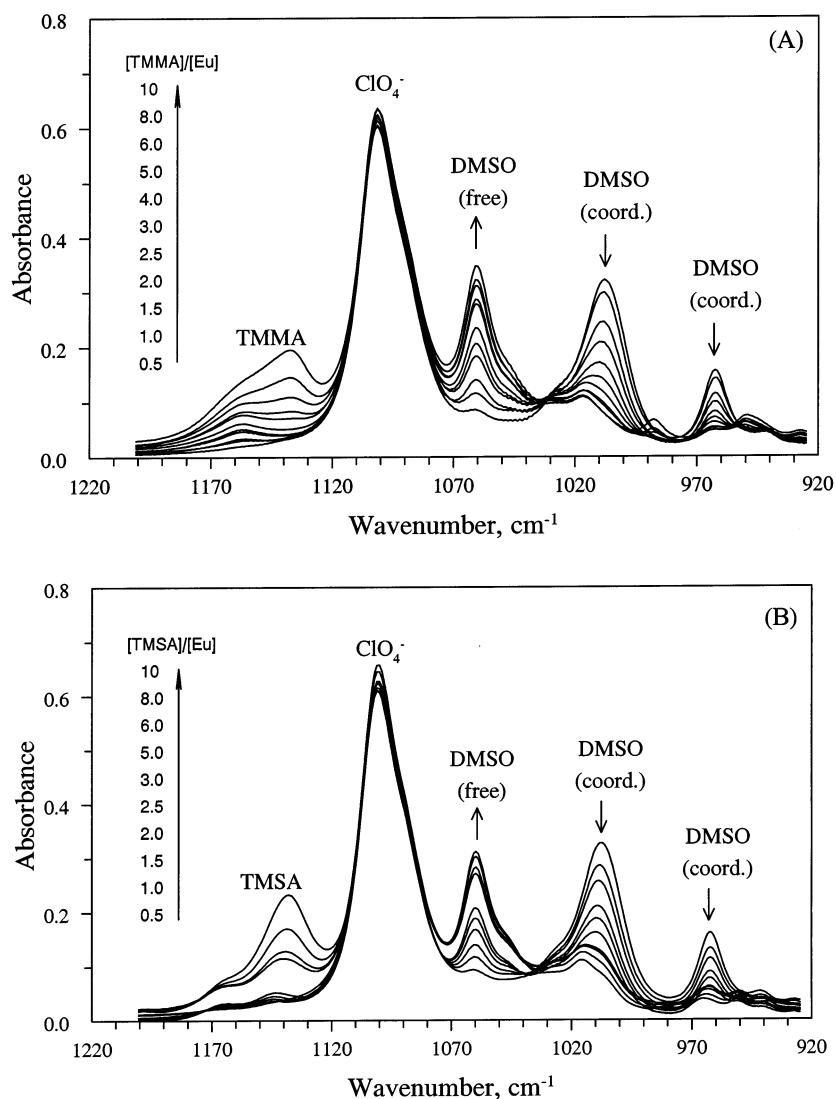
Fig. 7. FT IR spectra of Eu–diamides in AN containing small amounts of DMSO ([DMSO]/[Eu] = 7.2). The assignments of the bands are shown in Table 2. [Eu] = 33.3 mM. (A) Eu–TMMA, and (B) Eu–TMSA.

for quantitative measurements of the concentration of free DMSO in solution. Since neighboring bands can interfere with the accurate determination of the absorbance at 1060 cm^{-1}, the following curve fitting procedure was taken to perform quantitative analysis.

First, the IR spectra (in the range of 980–1200 cm^{-1}) of solutions containing different concentrations of DMSO (in the absence of Eu and diamides) were deconvoluted using three Lorentzian peaks around 1060, 1048 and 1016 cm^{-1}. The spectral decomposition revealed that the frequencies and the full widths at half height (fwhh) of these peaks were nearly constant in the concentration range of DMSO 30–990 mM. Based on this observation, a new series of spectral deconvolutions were carried out by maintaining these quantities constant and equal to the mean values (the frequency and fwhh are: 1059.58, 12.12; 1047.98, 18.15; 1016.10, 16.02 cm^{-1}). A calibration curve was then obtained by plot-

ting the calculated absorbance at 1060 cm^{-1} versus the concentration of DMSO in the solution. Finally, the experimental IR spectra (in the presence of Eu and diamides) shown in Fig. 7(A) and (B) were deconvoluted. Seven Lorentzian functions, including the three above-mentioned peaks that have fixed positions and fwhh values, were employed to simulate the experimental spectra of the solutions less concentrated in diamide ($C_L/C_M \leq 2$), while nine functions were necessary to simulate the spectra of more concentrated solutions. Two representative deconvolutions are shown in Fig. 8. The concentrations of free DMSO in the solutions containing Eu and diamides were calculated by using the calibration curve and the value of the absorbance at 1060 cm^{-1} obtained after spectral deconvolution.

The IR spectra for the system with [DMSO]/[Eu] = 5.0 were also collected. Trends similar to those for the system with [DMSO]/[Eu] = 7.2 as shown in Fig. 6 and

Fig. 7 were observed. Same deconvolutions were performed on the IR spectra of Eu–TMMA and Eu–TMSA in the system with [DMSO]–[Eu] = 5.0 to calculate the concentrations of free DMSO.

From the deconvoluted spectra, an average number of free DMSO per Eu(III) ion, $n_{\text{free DMSO}}$, defined as [free DMSO]/C_{Eu}, can be calculated. A plot of $n_{\text{free DMSO}}$ as a function of the average number of coordinated diamide ligand per Eu(III) ion, $\bar{n}$, defined as [coordinated diamide]/C_{Eu}, should reveal the number of DMSO molecules substituted by each diamide ligand when the Eu–diamide complexes form. Two plots for the systems of Eu–TMMA and Eu–TMSA with [DMSO]/[Eu] = 5.0 and [DMSO]/[Eu] = 7.2 are shown in Fig. 9(A) and (B). The plotted curves all have a linear part with a slope ca. 2 in the region of higher $\bar{n}$, suggesting both TMMA and TMSA are bidentate ligands and each replaces two DMSO molecules from the

coordination sphere of Eu(III). However, significant deviations from the straight lines are observed in the region of lower $\bar{n}$, indicating that fewer than two DMSO molecules are replaced by one TMMA or TMSA in this region. For the system with [DMSO]/[Eu] = 7.2, such deviations occur in the region where $\bar{n} < 1$, providing evidence that the formation of the first Eu–TMMA or Eu–TMSA complex does not perturb the solvating DMSO as much as the successive complexes do because there are about 1–2 'vacant' sites in the coordination sphere of Eu(III) in this solvent. This agrees very well with the reactions shown in Scheme II and supports the observations by calorimetry. In contrast, for the system with [DMSO]/[Eu] = 5.0, such curvature occurs in the region where $\bar{n} < 2$, providing evidence that the formation of EuL and EuL$_2$ (L: TMMA or TMSA) does not perturb the solvating DMSO as much as the successive complexes (EuL$_3$) do
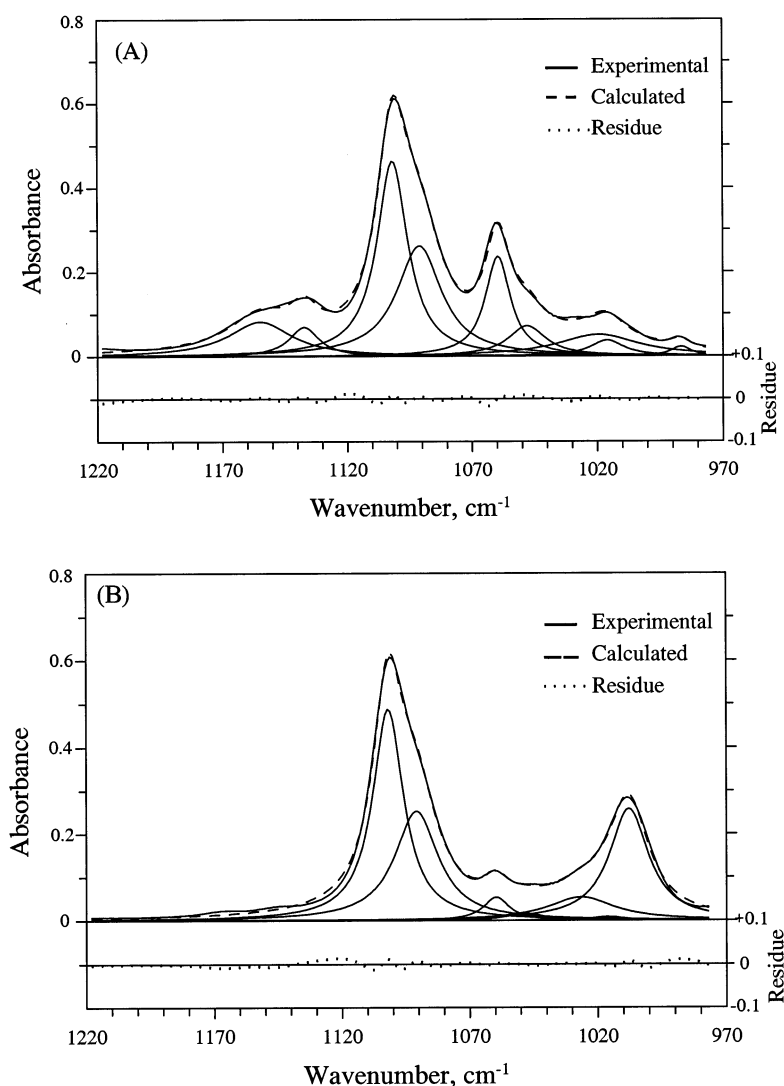

Fig. 8. Results of spectra deconvolution of Eu–amide systems in AN with [DMSO]/[Eu] = 7.2 and [Eu] = 33.3 mM. (A) [TMMA]/[Eu] = 8; (B) [TMSA]/[Eu] = 1.
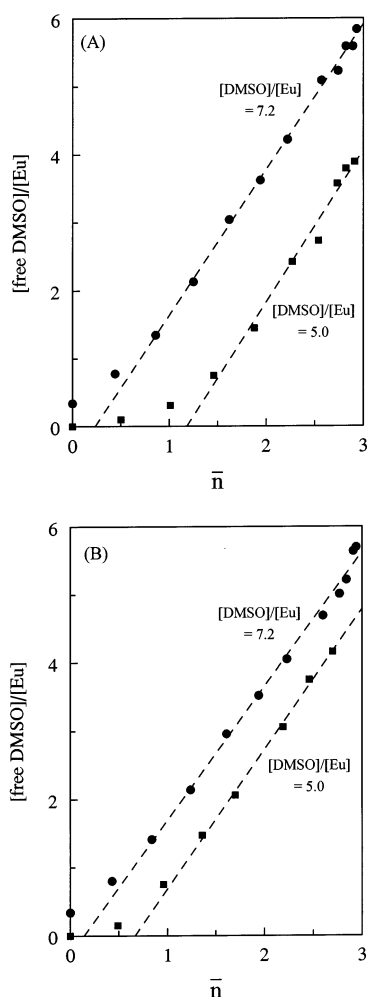
Fig. 9. Average number of free DMSO per Eu(III) ion, $n_{\text{free DMSO}}$, as a function of $\bar{n}$, the average number of coordinated diamides per Eu(III) ion. (A) Eu–TMMA; (B) Eu–TMSA. (●) in AN with [DMSO]/[Eu] = 5.0; (■) in AN with [DMSO]/[Eu] = 7.2.
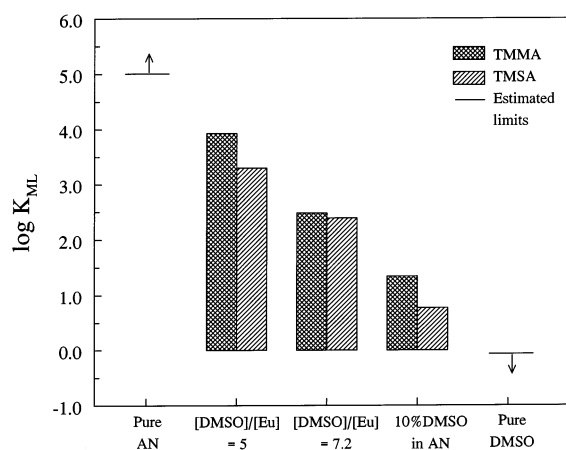

Fig. 10. Comparison of $\log K_1$ for Eu–TMMA and Eu–TMSA complexes in AN containing different amounts of DMSO.

because there are about 3–4 'vacant' sites in the coordination sphere of Eu(III) in this solvent. Again, this is

consistent with the results from calorimetry (Scheme III).

In summary, the FT IR results support the observations by calorimetry and are consistent with the enthalpy and entropy of complexation discussed previously.

3.4. Comparison between TMMA and TMSA

In pure AN or pure DMSO, the Eu–TMMA and Eu–TMSA complexes are either too strong or too weak to be quantitatively evaluated by calorimetric titrations. Only the lower or upper limits are estimated ($\log K_1 > 5.5$ in pure AN and $\log K_1 < 0$ in pure DMSO). Consequently, it is not possible to compare the binding affinity with Eu(III) between TMMA and TMSA in these two pure solvents. However, it has been demonstrated that, using AN containing small amounts of DMSO as the solvent, it is possible to measure the formation constants of these complexes and compare TMMA with TMSA. The formation constants (from Table 1) of the first Eu–diamide complex, Eu(TMMA) and Eu(TMSA), in various solvents are plotted in Fig. 10. As shown in this figure, TMMA forms stronger complexes than TMSA in all the three solvents of AN containing small amounts of DMSO.

The stronger binding affinity of TMMA to Eu(III) than TMSA can be attributed to the structural difference between these two ligands. Since both TMMA and TMSA form chelate complexes with Eu(III) through the carbonyl groups, the steric strain that is intrinsic in the formation of chelate rings must be considered. The more favored complex structures are those where the steric strain is at the minimum. In the absence of available data on the structure of the diamide complexes in solution, data on the crystal structure can be used to evaluate the steric strain in these complexes [9,25,60,61]. A comparison of the bond angles in the complexes reveals that higher steric strain is involved in the succinamide complex than the malonamide complex. For example, the Nd–O–C angles in the malonamide complex $\text{Nd(NO}_3)_3(\text{H}_2\text{O})_2(\text{DMPMA})$ [62] are 132.6 and 139.4° (Fig. 11(a)), while the Nd–O–C angles in the succinamide complex $\text{Nd}_2(\text{NO}_3)_6(\text{TMSA})_3$ [60] are 136.1 and 148.2° (Fig. 11(b)). The enlargement of the Nd–O–C angle in the latter implies that there is more stress in the succinamide complex. In addition, the C_1–C_2–C_3 angle in $\text{Nd(NO}_3)_3(\text{H}_2\text{O})_2(\text{DMPMA})$ (Fig. 11(a)) is 111.2° while the C_1–C_2–C_3 and C_2–C_3–C_4 angles in $\text{Nd}_2(\text{NO}_3)_6(\text{TMSA})_3$ are 114.2 and 114.8°. This means that a larger departure from the ideal tetrahedral configuration occurs on the methylene carbons in the succinamide complex than the malonamide complex. As a result, a higher degree of structural reorganization is probably required for succinamide than malonamide, thus a higher steric strain in the
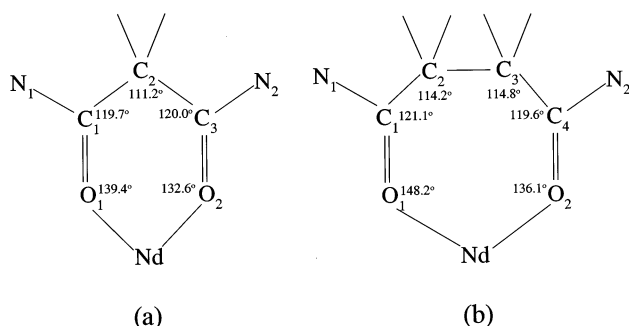
Fig. 11. Bond angles in Nd–malonamide and Nd–succinamide complexes. (a) $Nd(NO_3)_3(H_2O)_2(DMPMA)$, where DMPMA stands for *N,N′*-dimethyl-*N,N′*-diphenyl-malonamide [62]. The angles shown are the mean values found in the two molecules of the asymmetric unit [9]. (b) $Nd_2(NO_3)_6(TMSA)_3$ [60].

succinamide complex. Certainly, such steric strain could be a factor that makes the Eu–TMSA complexes weaker than the Eu–TMMA complexes.

Because the dicarboxylates can also form bidentate complexes with Eu(III) through two oxygen donors and there are plenty of data in the literature on the complexation of dicarboxylates with metal ions [63], it is informative to compare the diamides (TMMA and TMSA) with corresponding dicarboxylates (malonate and succinate). In aqueous solutions, the stabilities of metal dicarboxylates decrease as the chain length of the ligand acid increases (oxalate > malonate > succinate) [64], due primarily to an entropy effect. Longer dicarboxylate ligands suffer greater loss of rotational and translational freedom upon chelation than do shorter ones, hence a greater entropy loss [65]. However, the concomitant entropy gain caused by the release of water molecules from the hydration sphere of the metal ion is similar in all systems of dicarboxylate chelates. This type of entropy effect should also exist in the complexation of diamides in organic solvents and may contribute to the formation of stronger metal complexes with malonamide than succinamide. Though Table 1 shows that the difference in the entropy of complexation between Eu–TMMA and Eu–TMSA is not significant (within the error limits in most cases), the data for the system with [DMSO]/[Eu] = 5.0 do show a trend that the entropies of Eu–TMSA complexation are less positive than those of Eu–TMMA, an indication of greater loss of rotational and translational freedom for the longer chain bidentate ligand.

Acknowledgements

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